



A Synthesis of Structural, Morphological, Electrical and Dielectric property of *Manganese Dioxide* doped polyaniline [MnO₂/PANI]

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Abstract: The uniform distribution of (PANI) polyaniline and metal oxide composites is anticipated to enable the materials use in more applications. This work used APS (ammonium persulfate) as an oxidant and HCL used as catalyst to create PANI and manganese dioxide doped polyaniline (MnO₂/PANI) with various molar concentrations. Using the XRD and SEM techniques, the composites' structural and surface morphology were identified. Using "impedance analyzer" dielectric characteristics and the electrical (AC & DC) were formed. At room temperature, all of the composites' AC conductivity and dielectric constant were examined as functions of frequency, while the DC conductivity was temperature function.

Key Words: Manganese Dioxide/Polyaniline composite, Electrical conductivity, Dielectric and permittivity X-ray diffraction.

1. Introduction:

Conducting polymer, one of several materials, has special qualities including electrical, optical, and magnetic ones. This is why polymers are gaining more scientific and technological attention and providing the chance to create new polymer materials [1].

A conjugated structure with alternating single bonds as well as double bonds is the unique characteristic of conducting polymers. The characteristic that they all have is due to the similarity to the π -electron systems, which have better conductivity in either reduced or an oxidized state and may undergo reversible redox activation under the right atmosphere [2].

From the conducting polymers discovery, a brand-new, very promising area of engineering and materials science has developed. The most promising conducting polymers among them is conducting PANI, which has exceptional environmental stability, unique electrical, optical, and opto-electrical capabilities. Polyaniline is a chemical that may be utilized in electrochromic devices, secondary batteries, LED, electrostatic discharge protection devices, and other things [3-4].

Polyaniline stands out among all conducting polymers for its distinctive spectrum of electrical and dielectric characteristics as well as its high stability. With view of this, considering polyanilines as important material for fabricating the devices. Due to its high conductivity in a doped form, polyaniline (PANI) is a significant conducting polymer. PANI offers a broad variety of uses because of its flexibility in many fields. Solar cells, LEDs, sensors, radiation absorbers, and electromagnetic shields are a few examples of such applications. By doping metal oxide or other kinds of particles with polyaniline, it is possible to change the characteristics of PANI. It belongs to the class of materials known as PANI composites, in which conductivity is produced via a partial oxidation or reduction process. The green protonated emeraldine, is being formed by chemical oxidative polymerization process, is most significant of the various oxidation forms of polyaniline. When polyaniline is used to dope metal oxide or other kinds of particles, a charge-transfer process occurs in between the doped agent and PANI. When the removal of charge from the polyaniline through chemical doping, angles and the bond length alter. The charge is concentrated in place of many repeating units. Localized charges are considered as charge carriers in conducting polymers because they may move along the polymer chain. Due to its high degree of transparency in the visible spectrum, manganese dioxide is one of the most important materials. Nanoparticles of manganese dioxide are produced using a variety of chemical processes, including coprecipitation, hydrothermal, sol gel, sonochemical polymer, and precursor method. Conducting polymers, for example, have shown much greater specific capacitance at a low price. Numerous studies have been conducted on polyaniline (PANI), polypyrrole, polythiophene, and other compounds. In recent years, studies on the synthesis, characteristics, structure, and uses of PANI have been extensively researched. MnO₂ is a type of transition metal oxide that has been extensively explored. It is inexpensive, abundant, and environment friendly.

2. Materials and Method:

HCL (hydrochloric acid), Aniline, and analytical-grade APS are the substances utilized in the preparation of polyaniline and are produced by the chemical oxidative polymerization process.

i. Preparation of Polyaniline:

At 0°C, a 0.2M aniline solution as well as a 1N HCL solution are combined. For the purpose of completing the reaction, A magnetic stirrer was used to stir this mixture for two hours at a constant RPM. Ammonium persulfate solution 0.2 M was poured into the mixture drop by drop. For eight hours at a steady RPM and a temperature of 0° C, this reaction mixture was constantly stirred in a magnetic stirrer. The precipitate was filtered after 8 hours and thereafter washed with acetone and deionized water. The

final suspension was produced and then dried for 24 hours at 50° C. Black powder was produced as final product after grinding into powder [5].

ii. Preparation of MnO₂/Polyaniline:

At 0°C, a 1N HCL solution and a 0.2M aniline solution are combined. For the purpose of finishing the reaction, this solution had been stirred by a magnetic stirrer for two hours at a constant RPM. Drop by drop, the mixer was filled with the 0.2 M ammonium persulfate solution. For keeping the manganese oxide (MnO₂) powder uniformly suspended in the solution, several additive wt% (10%, 20%, 30%, 40%, and 50%) are adding to the mass fraction of the above solution while vigorously stirring. The finished solution was stirred for an additional 8H at 0°C. After eight hours, the filtered precipitate taken out and cleaned with acetone and deionized water. The final suspension is acquired when it dried for 24 hours in an oven at 50°C. A powder was formed from the final product [6].

3. Results and Discussions:

i. Structural Analysis:

A method called X-ray diffraction was used to examine the sample's structural analysis. According to the additive weight percentages (10%, 20%, 30%, 40%, and 50%), Fig 1 demonstrates the XRD pattern of the PANI MnO₂/PANI. Nature of polyaniline is amorphous. The pattern indicates that, the synthesized pure polyaniline shows that the prominent peak of pure PANI is in between the scale of 25 to 27° shows the properties of the PANI and conforms to the formation of PANI. Figures 2(b-f) showing the prominent peak of MnO₂ at 2θ values degree for different doping concentration (10%, 20%, 30%, 40% & 50%). Additionally, it has been shown that when doping concentration rises, the peak intensity grows from 800 counts to almost 40000 counts. This rise in the XRD peak's intensity may indicate that the manganese dioxide dispersion in the polyaniline matrix is still the same in broadness [7].

According to calculations made using the Debye-Scherrer formula, the typical crystalline size of PANI is expected to be about 17nm,

$$D = K\lambda / (\beta \cos\theta)$$

The lattice strain was calculated to be 0.0088, where D is the average crystalline size, X-ray wavelength denoted by λ, crystallite form factor denoted by K (a fair estimation is 0.9), β represents the X-ray diffraction peak's FWHM (Full Width at Half its Maximum), Bragg's angle (deg) denoted as 2θ and Estimated lattice strain is 0.0088.

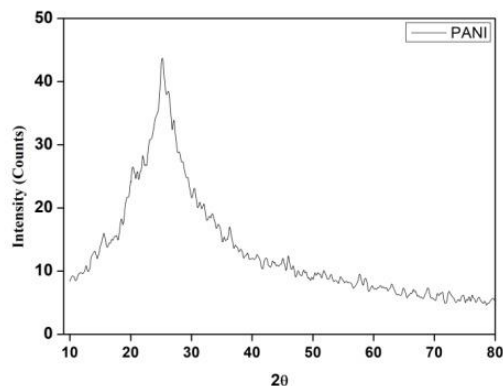


Figure-1: XRD pattern of PANI & Composite

ii. Morphological Study:

As shown in Figure 2, the surface morphology of pure PANI and MnO₂/PANI (10%, 20%, 30%, 40%, and 50%) respectively, are shown. The homogeneous shape and semi-crystalline-like structure of PANI are seen in the SEM picture. The effective formation of the composite is further shown by the MnO₂/PANI SEM image, which depicts the dopant metal oxide particles as being dispersed in PANI. The surface morphologies are mostly granular, nonporous, aggregated, and irregularly organized, with a variety of sizes. Additionally, it has been shown that the proportion of composites has little impact on the morphological image. The average grain size which was calculated was between 20–30nm [8–9].

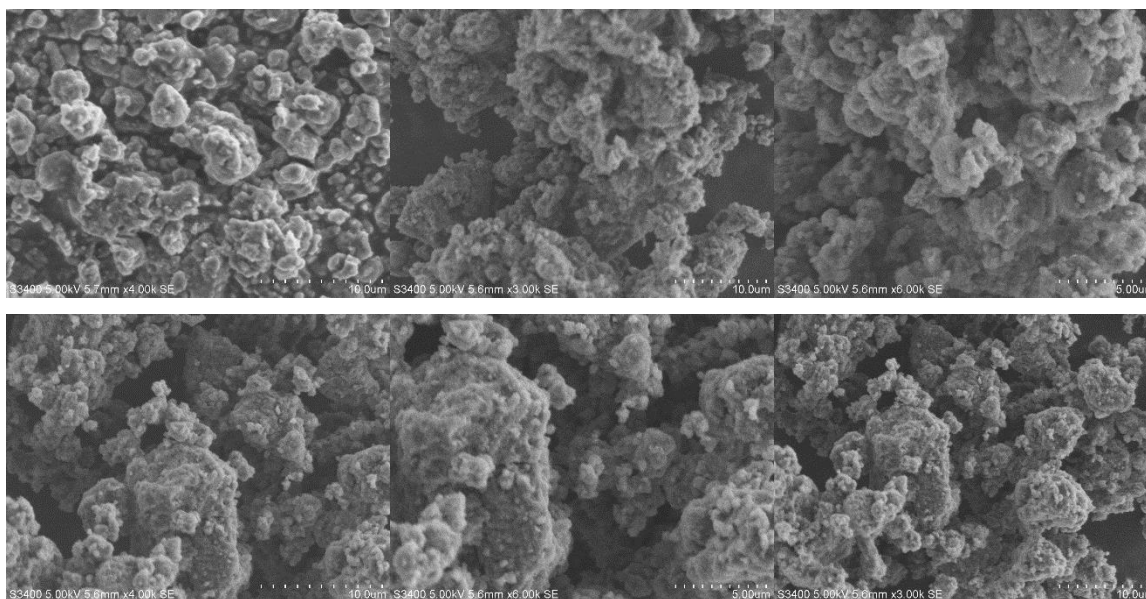


Figure-2: SEM image of PANI & Composite

4. Electrical Conductivity

a. AC Conductivity

The (electrical) AC conductivity of MnO₂/PANI composites and pure PANI was measured at room temperature between 1KHz and 1MHz frequency. Silver paste was applied on MnO₂/PANI pellets in layers varying in thickness from 2 to 5 mm. In Figure 3, the AC conductivity (σ_{ac}) as a function of frequency is shown for pure polyaniline and MnO₂/PANI (10%, 20%, 30%, 40%, and 50%) correspondingly. According to earlier reports, polyaniline's electrical conductivity varies from 10^{-10} to 10^3 S/cm according to the acid dopant along with the fillers [8]. It is discovered that when the frequency of polyaniline rises from 1KHz to 1MHz, its AC conductivity continuously rises. It is clearly evident that the AC conductivity depends on frequency and rises linearly with frequency. This suggests that there could be charge carriers capable of moving charges by hopping via defect sites throughout the polymer chain [9]. Additionally, graphs show that the conductivity also rises when manganese dioxide concentration rises from 10% to 50%, i.e., the conductivity is higher than pure PANI at 1KHz and 1MHz frequency. Figure 3 depicts the relationship between the added weight percents of manganese dioxide and the rise in conductivity of the PANI and composites. Figure 3 shows that, for both 1KHz and 1MHz frequency, the AC conductivity of PANI composite (50%) was shown to be better to all other composites. These composites' anomalous conductivity behaviour may be caused by a change in the Manganese Dioxide distribution in Polyaniline. As it was reported earlier, at 1 KHz, pure polyaniline's AC conductivity was determined to be at 3×10^{-7} S/m, and it increased to 6.5×10^{-6} S/m at 1MHz [10-11].

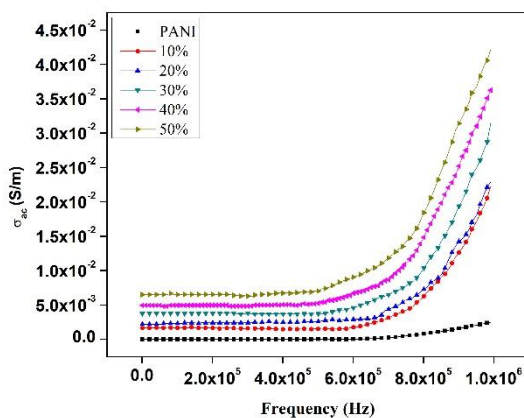


Figure-3: AC conductivity as a function of composition of PANI & MnO₂/PANI Composite

b. DC Conductivity

Temperature dependence of DC electrical conductivity of pure PANI and MnO₂/PANI composites was evaluated using silver paste coated pellets with a thickness range of 2 to 5 mm from room temperature to

180°C. For pure polyaniline and polyaniline composites, Figure 4 illustrates the fluctuation in Temperature-dependent DC electrical conductivity. DC conductivity of the PANI is determined to be 7.34×10^{-5} S/m at 30 °C and rises to 7.52×10^{-4} S/m at 180°C for pure PANI due to fact that this is true in all circumstances as temperature rises.

It is evident from the above, that when manganese dioxide content in the polyaniline matrix rises from 10% to 50%, conductivity decreases. The distribution of APS and manganese dioxide in polyaniline may be the cause of the reduction in dc conductivity. PANI conductivity is shown in two stages in the figure, with conductivity in the ranges of 30°C to 140°C as well as 150°C to 180°C. At intermediate temperatures, the first phase conductivity is often reported to be nearly constant, which is caused by the inter-chain transport of charge carriers, or the hopping of charge carriers among the polymer chains. The intra-chain transport of charge carriers, which can be explained by the band conduction mechanism and is typically identified at maximum temperatures, causes an unexpected and sudden conduction with rise in temperature in the higher temperature region (phase two) as stated by the researchers in their earlier study. The localised states that create structures resembling extended bands may work to trap the carriers from these states [12].

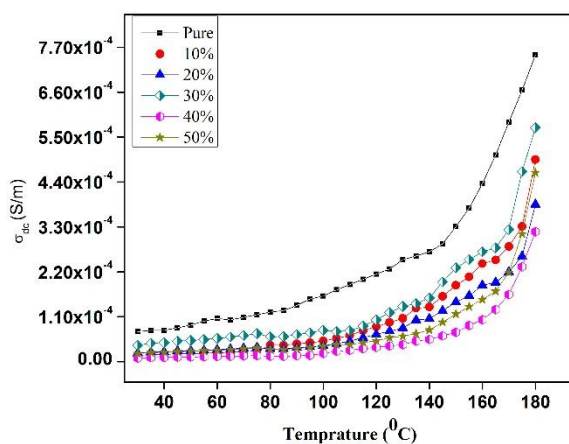


Fig-4: DC conductivity of PANI & MnO₂/PANI Composite

5. Dielectric constant

Figure 5 depicts the fluctuation of ϵ' as a frequency function for composites made of MnO₂/PANI and polyaniline (different wt%). The dielectric constant is shown to be relatively high in all cases at low frequencies and to decrease with increasing applied frequencies. The Debye relaxation process mechanism in these materials may be the cause of the observed behavior [13–14].

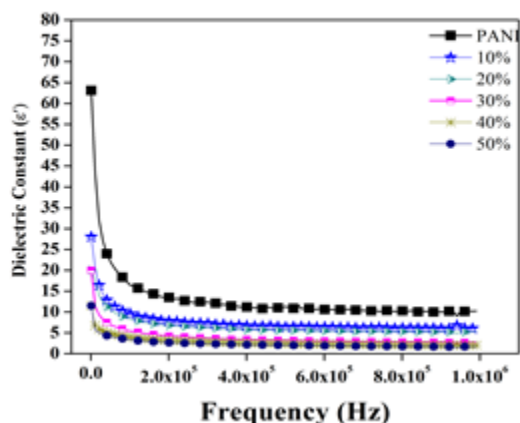


Figure-5: Dielectric constant of PANI & MnO₂/PANI Composite

6. FTIR analysis:-

The percentage of transmittance is represented as a function of wave number in cm⁻¹ in Fig 6a. IR spectra of pure polyaniline. Peaks in intensity may be seen in the IR spectrum at 3400, 2900, 2800, 1700, 1500, 1000, 700, and 550 cm⁻¹. The existence of C-N, C=N, and N-H stretching frequencies is being the reason of intensity peaks at 700, 1500, and 1000, respectively. The following factors may be responsible for the appearance of different bands in IR spectra [15-16].

Sample	Mode of vibration	Peak position (cm ⁻¹)
Pure PANI	C=N stretching	1500
	N-H stretching	1000
	C-N stretching	700

As shown in Fig. 6b, the Pure MnO₂ spectrum has prominent peaks at wave numbers of 3431 cm⁻¹, which are caused by the O-H vibration and are created at higher frequencies. The peak is at 2900 cm⁻¹ is caused by N-H stretching caused by the water molecule splitting on the surface of MnO₂ particles. The peaks is at 1601 to 1490 cm⁻¹ are caused by C-H in plane bending modes. The MnO₂ group may be responsible for the peak at 657 cm⁻¹, which is same to metallic stretch.

Sample	Mode of vibration	Peak position (cm ⁻¹)
Pure MnO ₂	O-H stretch	3431
	N-H stretch	2900
	C-H bending	1601 to 1490
	Metallic stretching	657

Fig-6c Demonstrate the spectra of PANI/MnO₂ composite shows a large broad band spectrum at 3434cm⁻¹

Which is because of the O-H stretch of the water molecules absorption; the peaks at 1793 and 1684cm⁻¹ are because of C=O aromatic stretch; the peaks at 1560 and 1451cm⁻¹ are due to the C-H stretch; the peaks from 960cm⁻¹ are due to alkene=C-H bending and peaks from 625cm⁻¹, are because of the metallic stretch[18-19].

Indicating that the MnO₂ particle distribution in the polymeric chain is homogenous, the typical stretching frequencies are shifted to the higher side of frequency. It might be explained by the attraction between MnO₂ and polymeric chains caused by the Vander walls force[20–22]..

Sample	Mode of vibration	Peak Position(cm ⁻¹)
PANI/ MnO ₂ composite	O-H Stretch	3434
	C=O stretch	1793&1684
	C=H bending	1560 to 1451
	Alkene=C-H bending	960
	metallic stretch	625

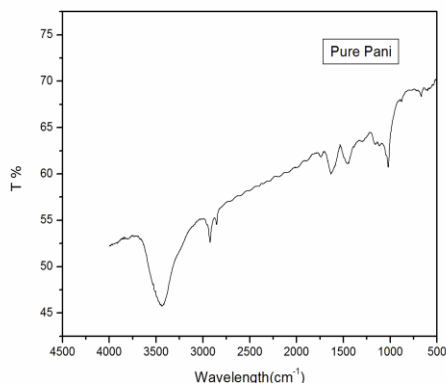


Fig 6a-FTIR of Pure Polyaniline

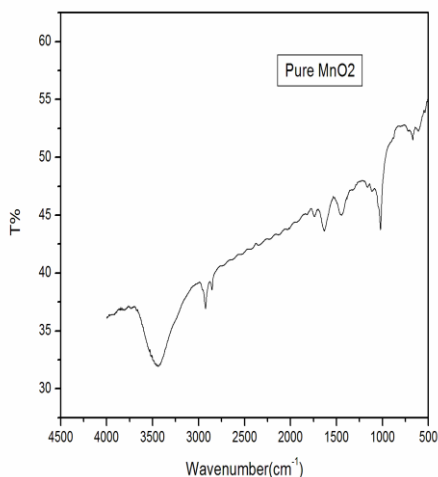


Fig 6b:- FTIR of pure MnO₂

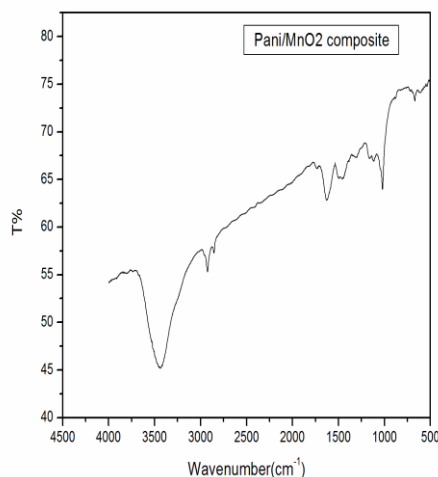


Fig 6c:- FTIR of PANI/ MnO₂ composite

6. Conclusion:

Polyaniline, a conducting polymer, and its composites, known as PANI, have been successfully synthesised in this work i.e .PANI / MnO₂, in 10, 20,30,40 & 50 weight percentages using chemical oxidative polymerization method. The polyaniline X-ray diffraction pattern reveals that polyaniline is amorphous and that polyaniline composites have well-ordered crystallinity. The SEM image of PANI reveals a shape that resembles a semi-crystalline structure.

The MnO₂/PANI SEM image shows that PANI is used to distribute the dopant metal oxide particles, which also explains how the composite was effectively formed. The surface morphologies are mostly granular, nonporous, aggregated, and irregularly organised, with a variety of sizes. Observed that the morphological image is not significantly affected by the proportion of composites. It is obvious that the AC(electrical)-conductivity depends on frequency and increases linearly with frequency. The DC conductivity of the PANI is seem to be 7.34×10^{-5} S/m at 30°C and rises to 7.52×10^{-4} S/m at 180°C for pure PANI, a result that is consistent in all situations. All of the above information makes it evident that when manganese dioxide content in the polyaniline matrix rises from 10% to 50%, conductivity declines. The dielectric constant is shown to be relatively high in all situations at low frequencies and to decrease with increasing applied frequencies.

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